

RESEARCH ARTICLE

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GreenCaps: towards solid curing agents for sustainable polyurethane foams

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Abstract

Testing and further investigation of organosilica microspheres functionalized with aqueous glycerol as solid curing agents for polyurethane (PU) foams confirms the potential of these materials to cure better and greener PU foams. The developed microspheres were found to be stable in the foam precursor mixture, allowing handling and mixing of the foam cans, and were shown to provide a slight improvement of the curing speed. The foams obtained from the froth containing the microspheres were found to maintain the level of quality of reference foam samples. Termed "GreenCaps", these microspheres will subsequently be tested in pre-commercial applications.

Keywords: Microencapsulation; Leaching; Polyurethane foam; Silica; ORMOSIL; Sol-gel; Curing agent; Glycerol

Introduction

Accounting for about 5% of all plastics produced worldwide, polyurethanes (PU) are among the most widespread polymer technologies [1]. Formed by reacting a di- or polyisocyanate with a polyol containing on average two or more hydroxyl groups, spray polyurethane foams (SPF) cured by atmospheric moisture are widely (and increasingly) [2] utilized in the construction industry for installing door and window frames, to seal gaps in roof constructions and to fix polystyrene and polyurethane panels to walls and insulate buildings.

Available in pressurized cans at retail locations and produced yearly at 500 million units, methylene diphenyl diisocyanate (MDI)-based one component polyurethane foam (OCF) is a self-expanding, adhesive gap filler cured by moisture [3]. In general, the pressurized can comprises a polyol blend added in the required amount for optimal curing up to the state in which no free isocyanate (-NCO) groups are present in the thermoset final polymer, namely the most important safety problem of the PU industry [4].

When it is fully reacted or "cured", the foam is stable and does not represent an health and safety hazard. However, the spray foam continues to react for some

hours afterward application when uncured isocyanates can cause skin, eye, and lung irritation, and chemical sensitization when absorbed through the skin [5].

We have recently described the use of mesoporous silica-based microspheres encapsulating aqueous glycerol as potential new curing agents affording the formation of OCFs of enhanced sustainability profile [6]. The use of glycerol as the polyol to cure PU foams in place of oil-derived monoethylene and diethylene glycols is both technically and environmentally convenient.

Renewable, non toxic glycerol today is entirely obtained from the biodiesel and oleochemicals industries; [7] while the higher amount of hydroxyl groups in the triol glycerol molecule (compared to diol glycols) results in both considerably lower percentage of free monomeric methylene diphenyl diisocyanate (MDI) and higher crosslinking density of the cured foam, which results in less curing shrinkage and less outflow of the sprayed material. It is also remarkable, from a green chemistry viewpoint, that the surfactant used to make the above mentioned silica microspheres, (namely sorbitan oleate, Span 80) is a biodegradable, non toxic ingredient derived from oleic acid and sorbitol, namely two natural products [8].

We now report the results of further testing of these materials under standard conditions. Results point to a number of findings of relevant practical value.

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Experimental section

We have lately reported elsewhere⁶ the preparation of the SiO₂ spheres (GC7), and of the 5% methyl-modified silica microparticles (CG8). The general scheme for the GreenCaps synthesis is displayed in Scheme 1.

In the following, we describe the standard test conditions developed at Greenseal Research Portugal, comprising 4 steps (A-D). In the first step, the shape and morphology of the MC is assessed via SEM microscopy.

The second step aims at assessing the presence of reactive agents on the surface of the microspheres. Mixtures of Ongronat 2500 (30% mMDI-70% pMDI) and selected amounts of dried microsphere sample CG8, namely (a) Ongronat 2500 + 0% CG8; (b) Ongronat 2500 + 2 wt % CG8; (c) Ongronat 2500 + 5 wt % CG8 are prepared.

The latter two mixtures are stirred gently with a spatula at room temperature for 5 minutes, until the microspheres are uniformly dispersed in the Ongronat isocyanates precursor blend. For comparison, we have also prepared a mixture of Ongronat 2500 with non-dried 2 wt % CG8, i.e. in a (decalin) slurry (mixture d). The viscosity of mixtures a, c and d is monitored every ca. 30 minutes, until 6 hours and then once a day (at least) until it reaches a *plateau* (or, in case of extensive leaching, the mixture solidifies).

In the third step, leaching in a PU formulation comprising a isocyanate and polyol blend (formulation 456, proprietary to Greenseal Research Portugal) is evaluated by adding the microspheres to the formulation, place it inside an aerosol can and pressurize it with propellants. The shaking rate (SR) is frequently assessed during the first 3 days. Constancy of the shaking rate indicates that there is no increase in viscosity inside the can and thus absence of leaching.

Finally, the mixture inside the can is sprayed through a valve in order to measure the froth output and evaluate the obtained froth, curing speed and the resulting foam quality. For example, the output is acceptable when it is above 4 g/s for a 395 mL can. The shelf life

target for commercial OCF cans is 1 year. Testing of the cans under accelerated conditions is possible by storing the cans in an oven at 45°C and spraying their content after 26 or 52 days, which corresponds to 6 months and 12 months ageing test.

Results and discussion

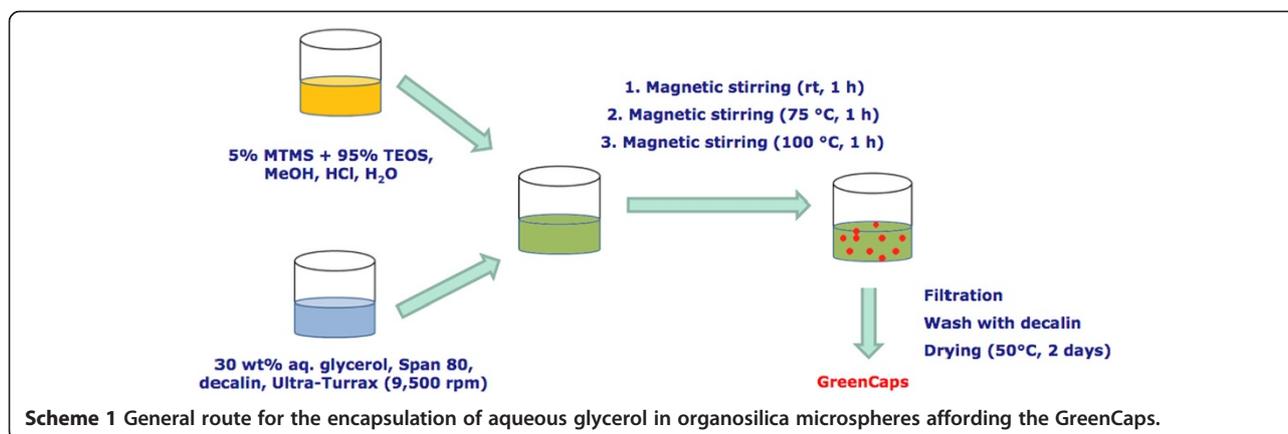
Figure 1 shows the SEM photomicrographs of dried 5%-methyl modified CG8 microspheres. The particles are perfectly spherical, well isolated and uniformly sized around 30 μm. Minor microparticle aggregation is inevitably found upon the mild drying step. However, such aggregation is truly limited, confirming the feasibility of these materials in light of forthcoming practical applications, as these microspheres are not expected to clog the valve during the spraying process.

The nature and amount of the microencapsulated species was assessed from dynamic thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Experiments were carried out under N₂ atmosphere using both doped and blank microspheres, as well as pure glycerol, decalin and surfactant Span 80 [9].

The amount of entrapped glycerol varies between 33 wt % for SiO₂ and 35 wt % for the CG8 sample confirming a consistent efficacy in the encapsulation of the hydrophilic glycerol molecules within the inner porosity in either the SiO₂ and ORMOSIL (organically modified silica) microspheres.

All samples have nearly 40 wt % residual inorganic content made of non porous SiO₂ formed upon condensation of all Si-OH at the surface, with water elimination and consequent loss of porosity. Finally, the TGA profiles of each sol-gel microsphere sample show that all microspheres encapsulate sorbitan monooleate within their inner porosity with almost constant 4% in weight of the microparticles being made of Span 80.

Figure 2 shows that after incorporating 2 wt % and 5 wt % of dried CG8 in Ongronat 2500, the increase in viscosity after 4 days in the isocyanate solution is rather



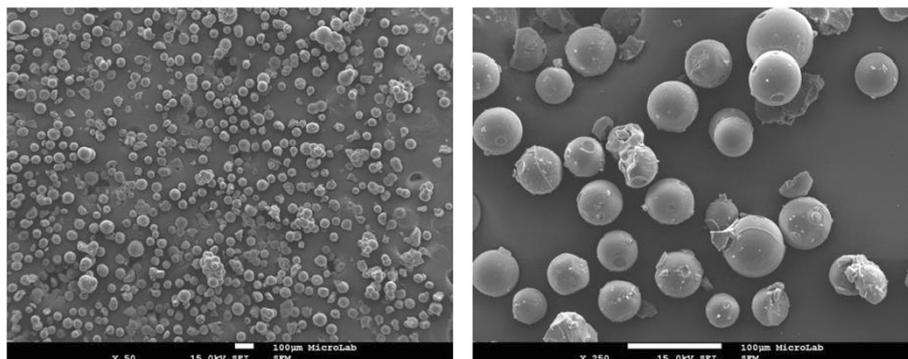


Figure 1 SEM photograph of 5% methyl-modified silica (CG8) dried microparticles doped with aqueous glycerol.

limited for the mixture containing 2 wt % CG8 microspheres.

On the other hand, a noticeable increase in the viscosity of the mixture is observed when a large 5 wt % amount of dried microspheres is employed, meaning that leaching occurs from inside the pores, which becomes discernible with the increase of the microspheres concentration from 2 to 5 wt %.

Remarkably, the increase in viscosity is significantly lower for dried microspheres compared to the same, but non-dried microspheres, supplied in a decalin slurry, which might be due to methanol, water or glycerol -OH groups emulsified in the decalin solution originating from the outer surface of the microspheres. The same trend (not reported in this paper) has been observed for

the SiO₂ microspheres and also for other ORMOSIL microspheres, with different methyl groups concentration.

The presence of methyl groups brings hydrophobicity to the microsphere material which helps in inhibiting leaching of hydrophilic aqueous glycerol from inside the pores.

Figure 3 shows a magnified graphical representation at the first hours of testing, exhibiting one plateau for mixtures (b), (c) and (d), ranging from ca. 1 and 4 h, which might be due to the reaction of residual OH groups present on the surface of the microspheres with the -NCO groups of the isocyanate blend during the first hour of mixture.

After 4 or 6 hours of mixture the viscosity restarts to increase, more or less significantly depending on the microspheres concentration, which is a result from some

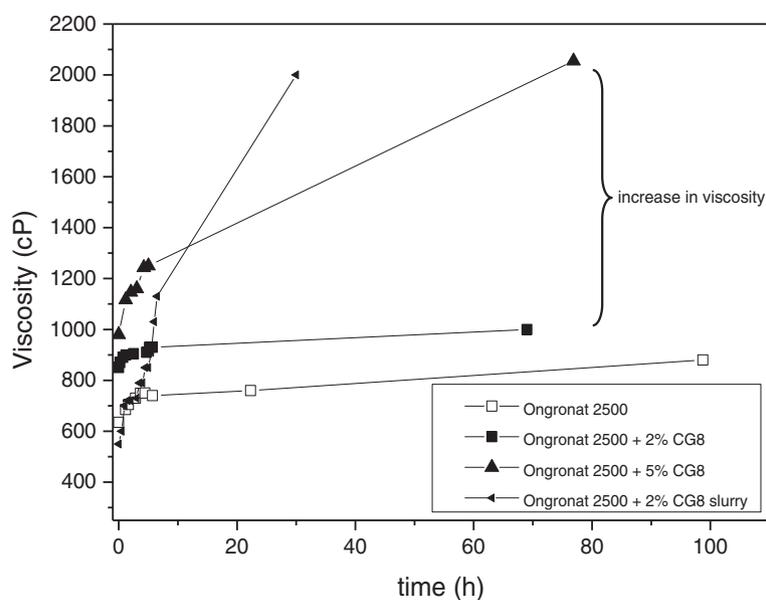


Figure 2 Viscosity temporal evolution of an isocyanate blend (Ongronat 2500) with and without organosilica microspheres, doped with aqueous glycerol, either dried (2 wt % and 5 wt % of CG8) or in a slurry (2 wt % CG8).

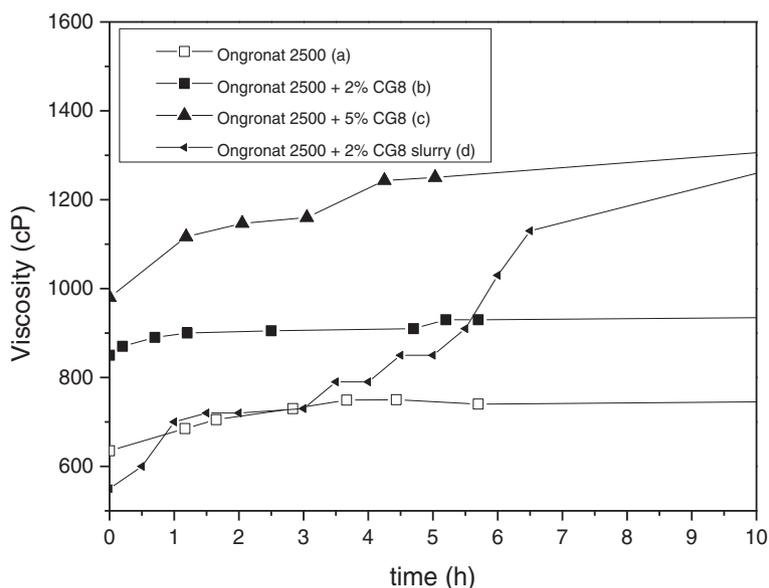


Figure 3 Viscosity temporal evolution of an isocyanate blend (Ongronat 2500) with and without organosilica microspheres, doped with aqueous glycerol, either dried (2 wt % and 5 wt % of CG8) or in a slurry (2 wt % CG8). Magnification of the graph of Figure 2, showing a plateau for the samples containing microcapsules.

leaching of OH species from the inside of the microspheres.

Mixture (b), which corresponds to dried microspheres, is the one showing less tendency for leaching whereas the mixture with the microspheres in a slurry (same concentration) is the one with more tendency to leach the entrapped aqueous glycerol content. It should be stressed that Ongronat 2500 without microspheres (a) exhibits a slight increase in viscosity due to the contact of $-NCO$ groups with the moisture in the air.

Having passed the preliminary test for leaching from the outer surface, the dried CG8 microspheres were added to the isocyanate + polyol proprietary blend Formulation 456. Taking into account the amount of entrapped aqueous glycerol in the microspheres obtained by TGA (35 wt %), we can determine the theoretical amount of microspheres CG8 required to fully cure the froth in a 0% relative humidity (R.H.) environment, which is found to be 29.4 g of CG8 microspheres for a 395 ml can (74 wt % related to the polyol blend).

It should be noted herein that only 8 g (20 wt %) of CG8 microspheres, were incorporated in the can, which is the amount of microspheres obtained in a single sol-gel synthesis on laboratory scale.

The cans were thus pressurized with the propellant at 6 bar and, remarkably, after 1 month of ageing at room temperature (23°C) all the cans were still shakable (shaking rate $SR \sim 1$, compared to $SR \sim 4$ for the reference can, i.e. without microspheres) meaning that there was a low increase in viscosity, but the can content remained liquid and, therefore, sprayable.

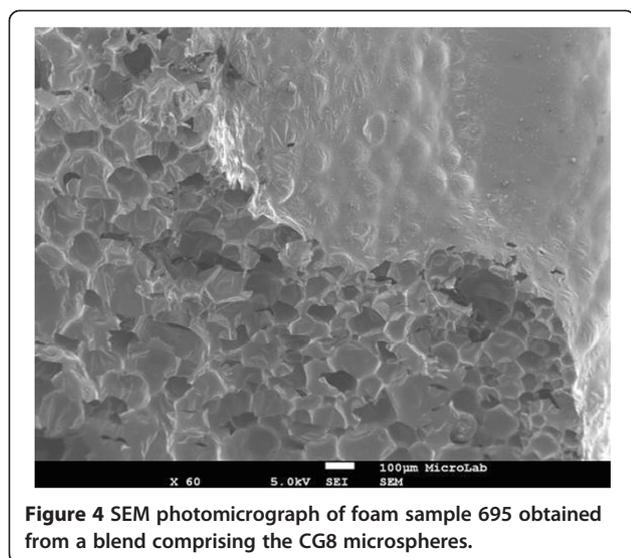
Table 1 shows the three parameters for curing speed evaluation (string time, tack-free time and cutting time). The “string” time is the time for which strings can no longer be pulled from the foam, “tack-free” time is the time when the final foam has lost its tackiness and can then be handled if required; and “cutting time” is the time it takes to become hard and dry enough to be possible to be cut with a knife. These are specifications provided by the manufacturer to end users of PU foam systems.

No significant difference in the string and tack-free time is observed. However, the foam with microspheres can be cut 5 minutes earlier than the reference sample (foam without microparticles), which means it is curing faster. The slight difference suggests that the amount of microparticles used in the test is not enough to produce a significant difference.

Indeed, the amount of microspheres used in the formulation should be higher, preferably ca. 74 wt % of the polyol blend (instead of the 20 wt % used in the present work) to result in a more visible effect, since the target is to reach a cutting time below 30 minutes. This will be tested in the future in order to enable the study of the

Table 1 Curing speed of PU foams sprayed from different cans at 23°C/40% RH

Foam #	String time (min)	Tack free time (min)	Cut time (h:min)
456 (without microspheres)	8	29	1:39
695 (with CG8 microspheres)	7	29	1:34



leaching behavior, curing speed and thixotropy of the froth in the presence of such a high quantity of ORMOSIL microspheres.

On the other hand, the quality of the foams obtained from the froth containing the microspheres was good and fully comparable to the reference sample and no microspheres or their residues are visible in the cured foam exhibited at the photomicrograph of Figure 4.

Indeed, even if the 20% amount of the MCs related to the polyol blend is about one fourth of the nominally required content, the complete absence of the microspheres cannot be justified by such a reduced amount. Ceramic microspheres might have the tendency for segregate away from the hydrophobic PU foam; or they might tend to deposit inside at the bottom of the can, releasing their content upon spraying, but not leaving the can.

Overall, these outcomes evidence a trend consisting of a faster curing in the presence of microspheres, but also of a tendency for a slow viscosity increase inside the can.

Conclusions

In conclusion, testing under standard conditions the newly developed mesoporous organosilica microspheres functionalized with aqueous glycerol in one component PU formulations shows that they are stable for prolonged time and can be smoothly sprayed affording PU foams of high quality, comparable to those obtained without microspheres.

With a rigid, ceramic porous structure these microspheres have mechanical properties good enough to be handled without extra care and to be mixed vigorously, without breaking, within the prepolymer mixture. Silica and organosilica ceramic microparticles functionalized with active organic species are emerging as high-performance

materials with application in widely different domains [10]. They do not swell, and once mixed with the polyurethane prepolymer mixture, the encapsulated water and glycerol molecules are not released during the storage of the cans for at least one month, for a concentration of 2 wt % of CG8 microspheres related to the isocyanate component. Instead, they lead to a slight improvement of the curing speed which, using one fourth of the required theoretical amount, is not yet enough for a practical application.

Named "GreenCaps", these microspheres will now be investigated in practical, pre-commercial applications aimed at using them as novel solid curing agents for polyurethane OCF formulations. Larger batches of microspheres will now be prepared and tested in terms of curing speed, foam quality and thixotropy of the froth thereby obtained. The concentration in the prepolymer blend will be tuned and optimized.

Competing interests

The authors declare that they have no competing interest.

Authors' contributions

RC devised the materials and prepared the microspheres. ACM carried out the experiments regarding leaching assessment, SEM analysis, polyurethane foams evaluation and gave support to the drafting of the manuscript. JCB gave support to the experiments planning and foams evaluation and to the drafting of the manuscript. ADS gave support to the testing of polyurethane foams and curing speed assessment. MP devised the materials and wrote the manuscript. All authors read and approved the final manuscript.

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